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(54) **Production of alkylene glycols**

(57) An alkylene oxide is converted to the corresponding glycol by reacting it with CO<sub>2</sub> in the presence of a

phosphonium halide in the substantial absence of water to produce the alkylene carbonate and reacting the carbonate with added water in the presence of the same catalyst to produce the glycol.

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## SPECIFICATION

## Production of alkylene glycols

The present invention relates to the production of alkylene glycols, especially ethylene glycol.

It is known from US Patent No. 2,994,705 that alkylene carbonates can be produced from

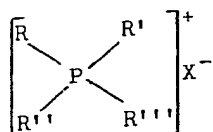
5 alkylene oxides by reacting them with carbon dioxide in the presence of phosphonium halides. 5

There is a substantial demand for alkylene glycols which is largely met by the direct hydration of alkylene oxides with water in the absence of a catalyst. This process produces the monomeric glycol together with polyglycols, the proportion of polyglycols increasing with the concentration of the product. If a high yield of the monoglycol is required, therefore, the reaction is carried out in the 10 presence of a substantial excess of water. The excess water must be removed in practise by distillation 10 if a concentrated glycol is required. So substantial an excess of water is not required when alkylene carbonates are converted to glycols.

It is also known from UK Patent Application No. 2,035,294 to hydrate alkylene oxides to the corresponding glycols by reacting them with water in the presence of quaternary phosphonium halides 15 and carbon dioxide. It is believed that the reaction proceeds through the formation of the alkylene carbonate as an intermediate. However, since the stoichiometric amount of water is present at the beginning of the reaction, a reaction leading to the formation of polyglycols proceeds in competition with that leading to the formation of the carbonate. In order to reduce this the quantity of catalyst must be high in order to maximise the rate of the desired reaction. The catalyst is however expensive. 20 Furthermore, the first step of the process is preferably carried out at higher pressures of CO<sub>2</sub> than the second. If hydration of the alkylene carbonate is to take place under the same conditions as its formation both steps of the process cannot be optimised. For this reason, we use a two stage process in which the production of the alkylene carbonate takes place in the substantial absence of water, and the alkylene carbonate is then decomposed in the presence of the same catalyst by adding water and 25 preferably reducing the pressure of carbon dioxide.

This invention therefore comprises a process of converting an alkylene oxide, especially ethylene oxide to the corresponding glycol by reacting the alkylene oxide with carbon dioxide in the presence of a phosphonium halide, there being substantially less, for example at least 75% less and preferably at least 90% less than an equimolar amount of water present based on the ethylene oxide, adding water to the 30 alkylene carbonate so produced and reacting it with the water in the presence of the same phosphonium halide to produce the glycol. 30

The phosphonium halide is suitably a quaternary phosphonium halide. It may be of formula



in which R', R'' and R''' are individually hydrocarbon or substituted hydrocarbon groups for example 35 alkyl, aryl, alkaryl, aralkyl or alkenyl groups and R can be hydrogen or preferably a hydrocarbon or substituted hydrocarbon group as aforesaid and X<sup>-</sup> is an iodide, bromide or chloride ion. Suitably the phosphonium ion comprises 4 to 60 carbon atoms and preferably 10 to 25 carbon atoms. 35

The partial pressure of carbon dioxide during the conversion of the alkylene oxide to the carbonate is suitably 10 to 50 bars. The temperature is suitably 120 to 300 and preferably 150 to 250°C.

40 The conversion of the carbonate to glycol may be carried out at a temperature of for example 130 40 to 300°C, preferably 150 to 220°C and more preferably 170 to 200°C. The pressure is suitably 0 to 50 bars absolute and for example 3 to 20 and more preferably at most 15, for example 5 to 10 bars absolute. The water concentration may be in the range 0.1 to 5 moles per mole of alkylene carbonate and is suitably about 1 mole per mole or is in an excess of at most 100% over the stoichiometric amount 45 required. 45

The amount of the phosphonium salt is suitably 0.01 to 50 and preferably 0.1 to 5 molar percent based on the alkylene oxide, carbonate and glycol present. In general bromide and iodide ions are more active than chloride ions and are preferred.

50 If quaternary phosphonium chlorides, bromides or preferably iodides are used as catalysts in the process when ethylene oxide is converted to ethylene glycol they may be recovered by an advantageous 50 method.

After distillation of the ethylene glycol product the catalyst remains as a residue which contains any polyethylene glycols produced, and may be recycled to the process directly or indirectly, for example to the ethylene carbonate production stage as previously mentioned. It is however necessary to remove 55 a purge of the residue to prevent the build up of polyethylene glycols in the process, and this purge may 55 be treated for recovery of the catalyst contained in it, optionally after distillation of diethylene glycol and if desired triethylene glycol, by adding water to precipitate the catalyst, for example in a ratio of 1:4 to 4:1 and preferably 1:2 to 2:1 parts of water per part of the residue by weight. Precipitation is suitably

carried out at a temperature of  $-10$  to  $50^{\circ}\text{C}$  and more preferably  $0$  to  $45^{\circ}\text{C}$ , a higher proportion of the catalyst being in general precipitated at lower temperatures. The precipitated catalyst may be recovered by for example centrifuging or filtering and re-used. If desired further catalyst remaining in this residue may be recovered by treating the residue with water after further concentration by distillation of polyethylene glycols from it or other suitable means, or the remaining residue may be discarded. Suitably the temperature during any distillation stages in which the catalyst is present is kept below  $300^{\circ}\text{C}$  and more preferably below  $250^{\circ}\text{C}$  to minimise decomposition of the catalyst.

#### EXAMPLE 1

A solution of ethylene carbonate (88 grams) containing the amount of methyltriphenylphosphonium iodide and water shown in Table 1 was charged in to a 300 ml stainless steel autoclave and carbon dioxide was introduced to give the stated total pressure in the autoclave. The mixture was heated to the temperature shown and the pressure maintained throughout the run. After the reaction time shown the product was analysed by gas chromatography and the selectivity to monoethylene glycol is indicated.

TABLE 1

$\text{MePh}_3\text{P}^+\text{I}^-$ (molar % based on EC)	Temp ( $^{\circ}\text{C}$ )	EC: $\text{H}_2\text{O}$ (moles)	reaction time (h)	Total pressure $\text{CO}_2$ (bars absolute)	EC conversion (%)	selectivity to MEG (%)
0.1	170	1:2	4	8 to 11	98.9	98.7
0.1	170	1:1.3	4	8 to 11	98.8	97.6
1.0	170	1:2	2	8 to 11	100	99.2
0.1	195	1:2	1	8 to 11	99.9	98.6
0.1	195	1:1.3	1	8 to 11	98.9	95.4
0.5	170	1:2	2	8 to 11	99.8	99.2
0	170	1:2	4	8 to 11	65	98.3
1.0	170	1:2	3	35 to 38	100	98.0
1.0	195	1:2	1	35 to 38	99.9	97.9

EC means ethylene carbonate  
MEG means mono-ethylene glycol

#### EXAMPLE 2

Recovery of methyl triphenyl phosphonium iodide from residues which would be expected in the reaction after distillation of mono and diethylene glycol was simulated by the following procedure.

The solution of methyl triphenyl phosphonium iodide (5 grams) in triethylene glycol (5 grams) was mixed with the amount of water shown in Table 2 at room temperature and cooled to  $5$  to  $10^{\circ}\text{C}$  over a period of one hour. Solid methyl triphenyl phosphonium iodide was precipitated filtered, washed with a little cold water and dried under vacuum. Its identity was confirmed by its melting point. In run number 5 the behaviour of a system in which the methyl triphenyl phosphonium iodide had been subjected to prolonged exposure to a temperature of  $170^{\circ}\text{C}$  in the course of distillations was simulated by heating a solution comprising 5 grams of methyl triphenyl phosphonium iodide, 5 grams of triethylene glycol and 0.5 grams of water to  $170^{\circ}\text{C}$  for 48 hours under nitrogen and then adding 5 grams of water at room temperature, chilling to  $5$  to  $10^{\circ}\text{C}$  and recovering methyl triphenyl phosphonium iodide as previously described.

TABLE 2

Run	wt water added (g)	recovery $\text{MePh}_3\text{P}^+ \text{I}^-$ (%)	mp $\text{MePh}_3\text{P}^+ \text{I}^-$ ( $^{\circ}\text{C}$ )
1	1	36.9	176—177
2	2	42.2	174—176
3	5	55.4	175—176
4	10	44.0	174—176
5	5.5	60.7	175—177

## EXAMPLE 3

- A 1 litre titanium autoclave fitted with a magne drive stirrer was charged with ethylene oxide (132 g, 3 moles), methyltriphenylphosphonium iodide (0.605 g, 0.0015 moles) and carbon dioxide to a pressure of 13 bars absolute at ambient temperature. The sealed system was heated to 180°C when the pressure reached a maximum of 30 bars absolute. A pressure of 21 bars absolute was maintained by  $\text{CO}_2$  addition until the formation of ethylene carbonate was complete (100 mins.). Water (108 g, 6 moles) was pumped into the reactor and the pressure reduced to 7.5 bars absolute. The pressure and temperature were maintained in the range 7.5 to 14 bars absolute and 160 to 180°C respectively until complete hydrolysis of the ethylene carbonate had taken place (3 hours). Gas chromatographic analysis of the resulting clear liquid showed monoethylene glycol to have been formed at 99.7% selectivity at a concentration of 10.74 mole per kg.

## COMPARATIVE EXAMPLE

## Single Stage Operation

- A 1 litre titanium autoclave fitted with a magne drive stirrer was charged with ethylene oxide (132 g, 3 moles), methyltriphenylphosphonium iodide (0.61 g, 0.0015 moles), water (108 g, 6 moles) and carbon dioxide to a pressure of 14 bars absolute at ambient temperature. The sealed system was heated to maintain the temperature in the range 148 to 156°C. The pressure rose to a maximum of 25 bars absolute and it was subsequently maintained at 21 bars absolute for 7 hours. Analysis of the clear liquid product showed that monoethylene glycol had been formed at a selectivity of 66.9% of monoethylene glycol, 10.3% ethylene carbonate remaining. The concentration of monoethylene glycol was 6.7 mole per kg.

## CLAIMS

1. A process of converting an alkylene oxide to the corresponding glycol which comprises reacting the alkylene oxide with carbon dioxide in the presence of a phosphonium halide, there being substantially less than an equimolar amount of water present based on the ethylene oxide, to produce an alkylene carbonate, adding water to the alkylene carbonate so produced and reacting it with the water in the presence of the same phosphonium halide to produce the glycol.
2. A process as claimed in Claim 1 in which ethylene oxide is converted to ethylene glycol.
3. A process as claimed in Claim 1 or 2 in which at least 90% less than an equimolar amount of water is present during the production of the alkylene carbonate.
4. A process as claimed in Claim 3 in which substantially no water is present during the production of the alkylene carbonate.
5. A process as claimed in any preceding claim in which the phosphonium halide comprises 10 to 25 carbon atoms.
6. A process as claimed in any preceding claim in which the phosphonium halide is a quaternary phosphonium iodide or bromide.
7. A process as claimed in any preceding claim in which the amount of phosphonium salt is in the range 0.1 to 5 molar percent based on the alkylene oxide, carbonate and glycol present.
8. A process as claimed in any preceding claim in which carbon dioxide is present at a partial pressure of 10 to 50 bars absolute during the first stage and in which the partial pressure of carbon dioxide is at most 15 bars absolute during the second stage.
9. A process as claimed in any preceding claim in which the production of the carbonate is carried out at a temperature in the range 150 to 250°C and the conversion of the carbonate to glycol is carried out at a temperature in the range 150 to 220°C.
10. A process as claimed in any preceding claim in which the catalyst is a quaternary phosphonium chloride, bromide or iodide and in which ethylene oxide is converted to ethylene glycol, in which ethylene glycol is distilled from the product, leaving the catalyst as a residue together with any

polyethylene glycols produced and in which the residue containing the catalyst is recycled to the process, in which a purge is removed from the residue and catalyst is recovered from the purge by adding water to precipitate the catalyst.

5 11. A process as claimed in any preceding claim whenever carried out as described with reference to any of the Examples. 5

12. Alkylene glycols whenever produced by a process as claimed in any preceding claim.

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